EVALUATION OF THE SLAG REGIME AND DESULPHURIZATION OF STEEL WITH SYNTHETIC SLAG CONTAINING Cr_2O_3

OCENA NAČINA DELOVANJA IN RAZŽVEPLANJE JEKLA S SINTETIČNO ŽLINDRO S Cr_2O_3

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The paper focuses on an evaluation of the slag regime and steel desulphurisation in a ladle with the help of synthetic slags based on Al_2O_3 containing various mass amounts of Cr_2O_3 varying from 0.3 % to 3.0 %. The aim of the plant experiments was to assess the achieved results when using two types of synthetic slag focusing on the course of desulphurisation, an analysis of the achieved chemical composition of the slag and an evaluation of the influence of oxide Cr_2O_3 on the increase in the chromium amounts in steel during secondary metallurgy. During the evaluation of the slag regime in the ladle, samples of steel from various technological nodes for a determination of the desulphurisation degree and the achieved chromium amounts in steel were taken. Samples of slags for the evaluation of the achieved chemical composition and amounts of Cr_2O_3 in the slag were also taken. The results mentioned in this paper represent the basic information about the possibilities of applying synthetic slags with increased amounts of Cr_2O_3 within secondary metallurgy.

Keywords: synthetic slag, desulphurisation, steel, secondary metallurgy

Članek obravnava oceno delovanja žlindre in razžveplanje jekla v ponvi z uporabo sintetične žlindre na osnovi Al_2O_3 in z različno masno vsebnostjo Cr_2O_3 od 0,3 % do 3 %. Namen industrijskih preizkusov je bil oceniti dobljene rezultate pri uporabi dveh sintetičnih žlinder z osredinjenjem na potek razžveplanja, analizo kemijske sestave dobljene žlindre in ocen vpliva oksida Cr_2O_3 na povečanje vsebnosti kroma v jeklu med postopkom sekundarne metalurgije. Med oceno delovanja žlindre v ponvi so bili postopoma vzeti vzorci jekla za določitev stopnje razžveplanja in dosežene vsebnosti kroma v jeklu. Vzeti so bili tudi vzorci za določitev kemijske sestave žlindre in vsebnosti Cr_2O_3 v žlindri. Doseženi rezultati so osnovna informacija o možnostih za uporabo sintetičnih žlinder s povečano vsebnostjo Cr_2O_3 pri postopku sekundarne metalurgije.

Ključne besede: sintetična žlindra, razžveplanje, jeklo, sekundarna metalurgija

1 INTRODUCTION

Slag regime in secondary metallurgy significantly influences the final quality of the produced steel, particularly with respect to the achieved desulphurisation of steel. One of the possibilities for influencing the slag regime is the application of synthetic slags to the ladle slag, formed from slag-making additions during the tapping of steel[1,2].

Synthetic slags are at present normally added to ladle slags in order to increase the quality of liquid steel by forming an active slag for an improvement of the kinetic conditions and refining processes. Added synthetic slags influence the properties of the ladle slag not only with its chemical and phase compositions, but also with the manner of their preparation and the granularity of the used raw materials. The aim of applying synthetic slags is to create a sufficiently basic and liquid slag with a low melting temperature, which contributes to an acceleration of the physical and chemical processes at the slag-metal interface, thus influencing the efficiency of metallurgical processes[3–5].

The paper is a follow-up of the other studies of the authors[6–8] and it presents industrial results and experiences with the use of briquetted synthetic slags based on Al_2O_3 and containing different mass amounts of Cr_2O_3 varying from 0.3 % to 3.0 %. The objective of the industrial experiments was to compare the results achieved with both types of synthetic slag, focusing on the evolution of desulphurisation, an analysis of the achieved chemical composition of the slag and an assessment of the influence of oxide Cr_2O_3 on an increase in the chromium in steel during the process of secondary metallurgy.

2 CHARACTERISTICS OF THE EXPERIMENTS AND SYNTHETIC SLAGS

Industrial experiments involving synthetic slags with different amounts of Cr_2O_3 were realised during the steel treatment in secondary metallurgy units (EAF→LF→ VD). Proper industrial experiments were realised during

Table 1: Chemical composition of steel St52-3 in mass fractions, *w*/%
Tabela 1: Kemijska sestava jekla St52-3 v masnih deležih, *w*/%

Grade	Range	Chemical composition (*w*/%)								
		C	Mn	Si	P	S	Cr	Ni	Mo	Al
St52-3	Min.	0.18	1.20	0.20	×××	×××	×××	×××	×××	0.020
	Max.	0.22	1.35	0.30	0.012	0.005	0.30	0.30	0.08	0.040

Table 2: Basic parameters of the used synthetic slags, *w*/%
Tabela 2: Osnovni parametri uporabljenih sintetičnih žlinder, *w*/%

Type of synthetic slag	Range	Chemical composition (*w*/%)					
		Al_2O_3	CaO	SiO_2	Cr_2O_3	MgO	Na_2O
A	Min.	60.0	10.0	3.0	×××	5.0	1.0
	Max.	70.0	12.0	4.0	0.3	7.0	2.0
B	Min.	60.0	9.0	2.0	2.0	3.0	2.0
	Max.	70.0	11.0	3.0	3.0	5.0	3.0

the production of steel grade St52-3 with the chemical composition given in **Table 1**.

During the evaluation period, a total of 184 heats of steel grade St52-3 were monitored, with both types of synthetic slags.

The production process ran in the following manner: during the tapping of steel from EAF into the ladle, an addition of the main part of the slag-making material (a mixture of lime and tested synthetic slags) took place. After the tapping, the ladle with steel and formed slag was transported to the ladle furnace (LF), where the targeted modification of the slag in the ladle was performed by adding the second part of the slag-making material (mainly lime). The production process was completed by casting steel into ingots[9].

For the evaluation of the influence of Cr_2O_3 on the slag regime in industrial conditions two types of briquetted synthetic slag, A and B, based on Al_2O_3 (*w* = 60–70 %) were chosen. Both types of synthetic slag were produced from secondary corundum raw materials with different mass amounts of Cr_2O_3 in the corundum raw material (*w* = 0.3 % and 3.0 %) and in combination with dolomitic lime and a binder (water glass). The main component was formed with Al_2O_3 and $CaCO_3$, which served as the source of CaO. Both types of synthetic slag were manufactured by briquetting and they were delivered in the standard manner in the form of briquettes with the dimensions of 60 mm × 50 mm × 30 mm. The basic chemical compositions of synthetic slags are presented in **Table 2**.

3 RESULTS AND DISCUSSION

The evaluation of the influence of synthetic slags containing Cr_2O_3 on the evolution of desulphurisation and the increase in the chromium amounts in steel was realised in several steps. First, an evaluation of the used synthetic slags according to their ability to desulphurise steel, determining the degree of desulphurisation η_s was made. The method of calculating the mentioned parameter was based on the previous studies[6,7,10]. It is evident

from the results of the degrees of desulphurisation (**Figures 1a** and **1b**) that individual average values representing different technological operations of steel treatment (EAF→LF→VD) obtained for the used synthetic slags A and B show different trends. That is why the results of the degrees of desulphurisation were obtained for the achieved amounts of sulphur at individual stages of the treatment (**Figures 2a** and **2b**).

It follows from the results (**Figures 1a** and **1b**) that the overall average degree of desulphurisation $\eta_S \Sigma$ for both synthetic slags, A and B, was approximately 93 %, which corresponds to the decrease in sulphur (**Figures 2a** and **2b**) from the average initial mass amounts of sulphur during the tapping that was 0.0401 % (synthetic slag A) and 0.0319 % (synthetic slag B) to the final mass amounts of sulphur after the vacuum treatment within the range of approximately 0.0027 % (synthetic slag A) and 0.0023 % (synthetic slag B).

It is also evident from the results that the average initial mass amounts of sulphur in steel differ within the range of 0.0082 %. This difference can be explained with the use of the charge material (steel charge) containing higher amounts of sulphur, namely, the heats with synthetic slag A.

During the first technological operation consisting of tapping steel from EAF into the ladle (LADLE) the lowest average degree of desulphurisation was achieved (**Figures 1a** and **1b**), η_S LADLE being approximately 23 % for both types of synthetic slag, A and B.

This trend can be explained with insufficient and only beginning dissolution of slag-making additions that are not able to desulphurise intensively[5]. During the tapping, a significant decrease in the steel temperature occurs, which also makes the conditions for steel desulphurisation worse. During the tapping of steel from EAF, the dosing of slag-making additions (the mixture of lime and tested synthetic slags), deoxidation of steel, deactivation of slag and partial alloying of steel take place.

During the tapping of steel into the ladle, a sequential stirring and dissolution of individual components occur.

That is why during the stirring, the liquidus temperature of the mixture of oxides gradually decreases, until a partial, or local, melting of the ladle slag is achieved, which partly participates in desulphurisation of steel in a short interval lasting from 3.5 min to 7 min.

It follows from the results (**Figures 1** and **2**) that the main part of desulphurisation of steel took place during the treatment of steel in the ladle furnace, LF, and in the vacuum unit, VD.

During the treatment of steel in the ladle furnace, LF, a triple increase in the degree of desulphurisation, η_S LF, takes place in comparison with η_S LADLE. For synthetic slag A the achieved average degree of desulphurisation, η_S LF, was approximately 66 %, and in the case of synthetic slag B the average degree of desulphurisation, η_S LF, was approximately 72 % (**Figures 1a** and **1b**). Degrees of desulphurisation, η_S LF, had different values, but the average drop in the mass amounts of sulphur in steel was at the same level, in the range of 0.0207 % (synthetic slag A) and 0.0202 % (synthetic slag B).

A significant increase in the degree of desulphurisation, η_S LF, and a uniform difference in the amount of sulphur in steel can be explained with the dissolution of slag-making additions, modification of the chemical composition of the slag due to the second dose of slag-making additions, together with the material for protecting the lining, calcium carbide and aluminium in various forms. It is also possible to state that a higher degree of desulphurisation, η_S LF, of approximately 6 % for synthetic slag B is caused by the lower initial amounts of sulphur in steel at the beginning of the steel treatment in the ladle furnace for the heats where synthetic slag B was used.

During the last technological operation, the treatment of steel in the vacuum unit, VD, another significant desulphurisation takes place (**Figures 1** and **2**). In the case of synthetic slag A, the degree of desulphurisation, η_S VD, was approximately 73 %, and in the case of synthetic slag B the achieved degree of desulphurisation, η_S VD, was approximately 62 % (**Figures 1a** and **1b**). The achieved degrees of desulphurisation of steel in both synthetic slags, A and B, can be explained with the complete dissolution of slag-making additions, a relatively higher temperature of steel and intense stirring of steel with the refining slag during the process of vacuum treatment, which has a big impact on the kinetic conditions of steel desulphurisation.

In the case of synthetic slag B the degree of desulphurisation, η_S VD, decreased by approximately 11 % in comparison with synthetic slag A. This lower degree of desulphurisation was reflected also by a lower decrease in the mass amounts of sulphur in steel. The average values were 0.0051 % for synthetic slag B and 0.0076 % for synthetic slag A. This trend can be explained with the amounts of sulphur in steel that were lower by one third at the start of the treatment in the vacuum unit, VD, when using synthetic slag B. The final slag mixture of both types of synthetic slag, A and B, formed in the course of the treatment in the ladle furnace, LF, and in the vacuum unit, VD, can be characterised as a liquid
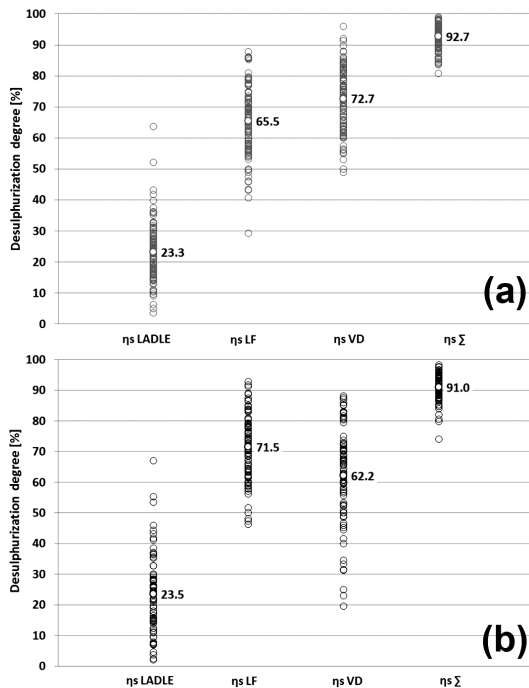

Figure 1: Obtained degrees of desulphurisation at individual stages of steel treatment
Slika 1: Dosežena stopnja razžveplanja pri posameznih stopnjah obdelave jekla
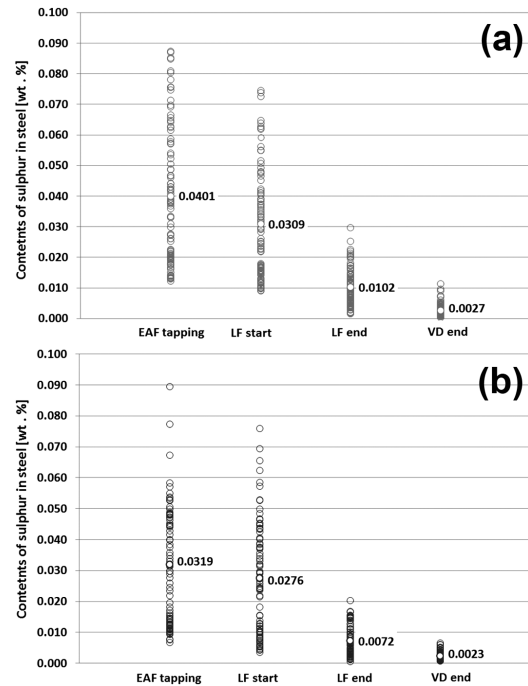

Figure 2: Obtained contents of sulphur at individual stages of steel treatment
Slika 2: Dosežena vsebnost žvepla pri posameznih stopnjah obdelave jekla

Table 3: Achieved chemical compositions of ladle slags, *w*/%
Tabela 3: Dosežena kemijska sestava ponovčnih žlinder, *w*/%

Synthetic slag A (*w*/%)				Synthetic slag B (*w*/%)			
LF$_{START}$		VD$_{END}$		LF$_{START}$		VD$_{END}$	
CaO	53.83	CaO	58.64	CaO	53.26	CaO	57.30
Al$_2$O$_3$	26.87	Al$_2$O$_3$	25.95	Al$_2$O$_3$	28.76	Al$_2$O$_3$	27.73
SiO$_2$	7.96	SiO$_2$	6.88	SiO$_2$	6.55	SiO$_2$	6.17
MgO	7.76	MgO	5.15	MgO	7.54	MgO	5.80
S$_{slag}$	1.16	S$_{slag}$	1.55	S$_{slag}$	0.99	S$_{slag}$	1.10
FeO	0.79	FeO	0.52	FeO	0.87	FeO	0.47
MnO	0.41	MnO	0.15	MnO	0.78	MnO	0.19
Cr$_2$O$_3$	0.05	Cr$_2$O$_3$	0.02	Cr$_2$O$_3$	0.04	Cr$_2$O$_3$	0.02

refining slag, which participates in a significant manner in the reactions between the slag and the metal.

The chemical composition of slag also influences desulphurisation during secondary metallurgy. That is why an evaluation of the changes to the chemical composition of the ladle slags using synthetic slags A and B was made. The achieved average results for the chemical composition of ladle slags are given in **Table 3**.

According to the data in[11–14] the calcium-alumina slag is considered to be the optimum refining slag for the steel deoxidised with aluminium and determined for secondary metallurgy. It should contain the following proportions of oxides in mass fractions: 55–60 % of CaO, more than 25 % of Al$_2$O$_3$, less than 6 % of SiO$_2$, 3–8 % of MgO and less than 1 % of FeO.

It follows from the average values (**Table 3**) that the optimum composition of the ladle (refining) slag was achieved when using both types of synthetic slag, A and B. It also follows from the results (**Table 3**) that the first dose of slag-making additions formed a ladle slag, whose chemical composition corresponds to the optimum composition. However, after tapping, this slag created in the ladle was only partially dissolved. After its arrival to the ladle furnace, LF, the slag was modified due to the second dose of slag-making additions. The aim was to increase the amount of lime (CaO) in the slag, as well as to deactivate the slag (a reduction of the amounts of easily reducible oxides). Subsequently, the heating and dissolution of slag-making additions occurred. In this manner a liquid refining slag was formed in the ladle furnace (LF), with which it was possible to achieve a high degree of desulphurisation during the treatment of steel in secondary-metallurgy units.

The next part of the evaluation of the results consists of an assessment of the influence of synthetic slags A and B containing Cr$_2$O$_3$ (in the range of mass fractions from 0.3 % to 3.0 %) on the increase in the chromium amounts in steel. It is possible to assume that it is reduced (with the element with the highest affinity to oxygen), and steel is fouled with chromium. Aluminium as the most suitable reduction agent was chosen and added in the form of Al$_{ingots}$ (a deoxidation agent), and also in the form of Al$_{skimming}$ and Al$_{granular}$ (a slag-deac-

tivation agent)[15,16]. The theoretically possible maximum reduction thus takes place during the reaction with the dissolved aluminium added during the tapping of steel into the ladle (the first dose of slag-making additions) or in the ladle furnace, LF (the second dose of slag-making additions) in accordance with the following equation:

$$(Cr_2O_3) + 2Al \rightarrow (Al_2O_3) + 2[Cr] \qquad (1)$$

By substituting the molar masses of individual components in equation (1) it is possible to determine, from the information from the heat records, the maximum theoretical contribution of chromium to steel. In the case of synthetic slag A ($w(Cr_2O_3) = 0.3$ %) it is possible to determine, on the basis of equation (1) with the substituted molar masses of individual components that the average maximum theoretical increase in chromium should be $5 \cdot 10^{-6}$. Using equation (1) it is possible to determine for synthetic slag B ($w(Cr_2O_3) = 3.0$ %) that the average maximum theoretical increase in chromium should be $48 \cdot 10^{-6}$.

It is evident from the amounts of chromium in steel (**Figure 3**) that in the heats with synthetic slag B its average amount in steel after the tapping from EAF into the ladle was lower by $249 \cdot 10^{-6}$ than in the heats with synthetic slag A. It is possible to assume that this distinct difference is due to a different (lower) quality of the used steel charge in the case of synthetic slag A, which was
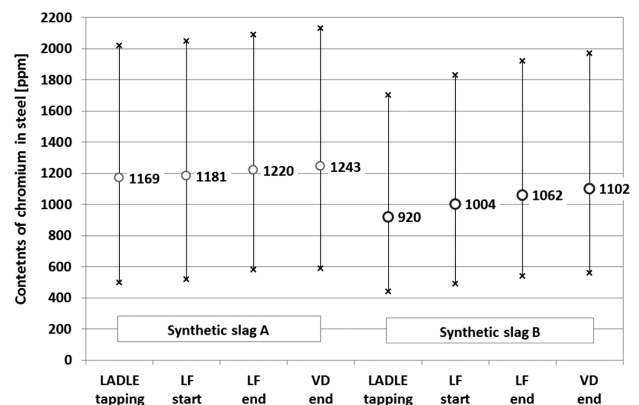

Figure 3: Chromium amounts obtained during the treatment of steel
Slika 3: Dosežene vsebnosti kroma med obdelavo jekla

manifested also by higher initial amounts of sulphur in steel compared to synthetic slag B.

It follows from the achieved results (**Figure 3**) that in the heats with synthetic slag B a significant increase in the amounts of chromium occurs during all the technological operations (EAF→LF→VD). The biggest differences between these amounts occur during the tapping and during the transport of the ladle to the ladle furnace, which can be explained with the dissolution of ferroalloys, slag-making additions and deoxidation additions during the tapping and the subsequent heating at the beginning of the treatment in the ladle furnace. The lowest increases in the chromium amount in steel occur in the vacuum unit, when, during this operation, the liquid refining slag is already formed and the main objective is the reduction of the sulphur mass amounts in steel below 0.005 % and the reduction of the gas amounts in steel (hydrogen and nitrogen).

It also follows from the results (**Figure 3**) that the average increase in the chromium amounts during the treatment of steel (EAF→LF→VD) when using synthetic slag A was $74 \cdot 10^{-6}$, and in the case of synthetic slag B, its average value was $182 \cdot 10^{-6}$. If we deduct from these values that the calculated maximum theoretical increase in the chromium amount for synthetic slag A was approximately $5 \cdot 10^{-6}$ and for synthetic slag B it was approximately $48 \cdot 10^{-6}$, we get the average increase in the chromium amounts in steel from other sources, in addition to the synthetic slags that are present. For the heats with synthetic slag A this increase was $69 \cdot 10^{-6}$ and for the heats with synthetic slag B it was $134 \cdot 10^{-6}$.

In the case of the heats with synthetic slag B used during secondary metallurgy, apart from the added synthetic slag, approximately twice the quantity of chromium is also reduced in steel (after a deduction of chromium from the synthetic slag) compared to the heats with synthetic slag A. Possible sources of chromium may be, for example, overflown furnace slag or ferro-alloys containing chromium. Another important source may be also the chromium that penetrated to the ladle lining from the previous heat alloyed with chromium (e.g., 42CrMo4 or 34CrNiMo6).

It may be also stated that the chromium mass amounts in steel in the case of both synthetic slags achieved the values of 0.12 % (synthetic slag A) and 0.11 % (synthetic slag B) and they are considerably lower than the required maximum chromium amount for steel St52-3, which is 0.30 %. The application of synthetic slags A and B caused a certain increase in the chromium amount in steel, but it follows from the results that the quality of the used charge had a pronounced influence on the chromium amounts in steel.

4 CONCLUSIONS

In industrial conditions a series of experimental heats were used with the aim of getting information about the influence and behaviour of two types of synthetic slags containing different mass amounts of Cr_2O_3 varying from 0.3 % to 3.0 %. On the basis of the obtained results of the industrial experiments it is possible to define the following findings:

When using both synthetic slags a very high degree of steel desulphurisation is achieved, which varies between approximately 91 % and 93 %. During the steel treatment in the ladle furnace and vacuum unit, the main part of steel desulphurisation took place. This can be explained with a complete dissolution of the first and second doses of slag-making additions, a modification of the chemical composition of the ladle slag and a relatively higher temperature.

The optimum composition of the ladle (refining) slag was obtained with both types of synthetic slag. The first dose of slag-making addition made it possible to create a ladle slag which was only partially dissolved. After the slag modification due to the second dose of slag-making additions to the ladle furnace and after the heating, the dissolution of slag-making additions took place.

The obtained chromium mass amounts in steel were 0.12 % (for synthetic slag A) and 0.11 % (for synthetic slag B) and they were considerably lower than the maximum allowed amount of chromium for steel St52-3, which is 0.30 %.

Our attention in the next stage of the research will be focused on confirming these industrial results during the production of different steel grades with higher amounts of chromium when using synthetic slag B.

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